Upgrading Biomass-derived Oxygenates to Fuels and Chemicals using liquid phase hydrogenations

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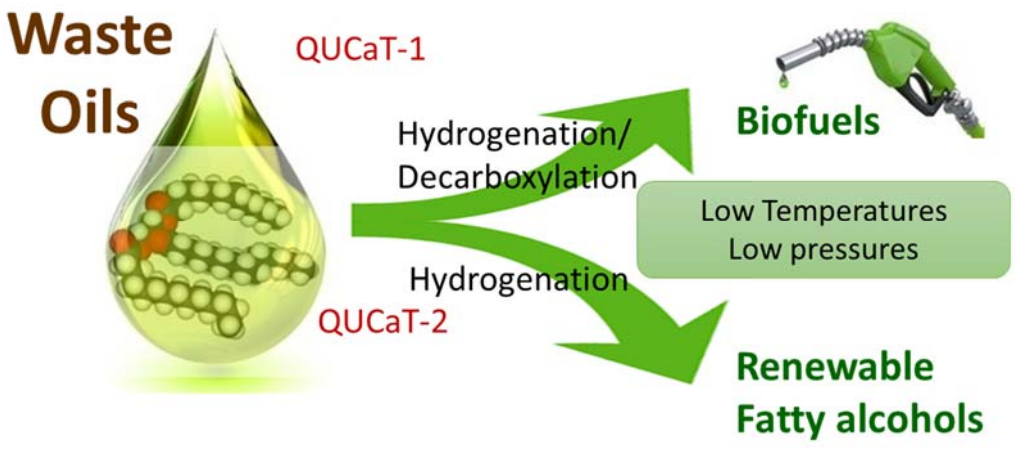
Catalysis is an enabling technology, playing a key role in sustainable, environmentally benign manufacture of renewable chemicals and biofuels. It is possible to design new and improved catalysts and catalytic processes to enhance activity and product selectivity by using multi-disciplinary approach, by understanding the mechanistic interactions at molecular level, by combining reaction kinetics, *in situ* spectroscopy and molecular modelling. A holy grail in catalysis is to establish rational design criteria for development of robust catalysts with high efficiency, selectivity and longevity. In our research group, we have established rational design criteria by using exemplar chemical processes such as hydrogenation of various arenes, aldehydes, ketones, fatty acids and vegetable oils. The insights obtained from theory and experiments were combined to establish rational design criteria for development of new catalysts. We have obtained new insights into control of selectivity of either C=C or C=O double bond using a variety of exemplar aldehydes, ketones, fatty acids and functionalized furanics.

Hydrogenation of fatty acids feedstocks into renewable hydrocarbon based drop-in biofuels and bio alcohols has been the subject of a significant amount of attention due to the potential to add significant value to biomass (Figure 1). This is currently performed industrially on a large scale using catalytic hydrogenation; however, the commercial processes typically utilise high pressures (up to 200 bar H_2) and temperature (up to 250 °C). At Queen's University, we have developed a new low temperature catalytic technology which allows the reactions to be performed under low temperature (60-130 °C) and low hydrogen pressure (1-30 bar) using novel tri-metallic catalysts (QUCaT-1). The QUCaT-1 technology not only promotes the reaction rates under mild conditions, but also enhances the selectivity to corresponding alcohols (>95% selectivity at ~100% conversion of fatty acid), as compared to an unpromoted catalysts. We have also tuned the composition of the catalyst to selectively produce corresponding hydrocarbons for use as biofuels.



We have also developed selective hydrogenation processes for reduction of ketoisophorone and cinnamaldehyde as the exemplar aldehydes and ketones by using manganese oxide octahedral molecular sieves (OMS-2) and Pt/OMS-2 catalysts [1,2]. We were also able to achieve selective hydrogenation of halogenated arenes to corresponding reduced arenes without dehalogenation [3]. High selectivities for reduction of C=C, 97% selectivity to levodione at 100% conversion were achieved by using OMS-2 and platinum supported on OMS-2 catalysts. In the case of cinnamaldehyde hydrogenation using Pt/OMS-2, reduction of C=O double bond was favored forming cinnamyl alcohol with 80% selectivity at 96% conversion. Density functional theory (DFT) calculations showed the dissociation of H_2 on OMS-2 was water assisted and occurred on the surface Mn of OMS-2(001) modified by an adsorbed H_2O molecule. For the first time, an *in situ* study on the interaction of molecules with a supported metal catalyst in a pressurized reactor by means of X-ray absorption spectroscopy (XAS). This approach to the best of our knowledge has never been used to evaluate the influence of adsorbed molecules on the electronic structure of the active site in the liquid phase [Figure 2]. The change in the Pt electronic structure following the adsorption of ketoisophorone and cinnamaldehyde was followed by *in situ* XANES. This demonstrates, for the first time, that, the combination of state-of-the-art spectroscopy (HERFD-XANES) and theoretical calculations is a powerful and versatile tool to reveal differences in adsorption behavior for reactants in liquid phase under reaction conditions.

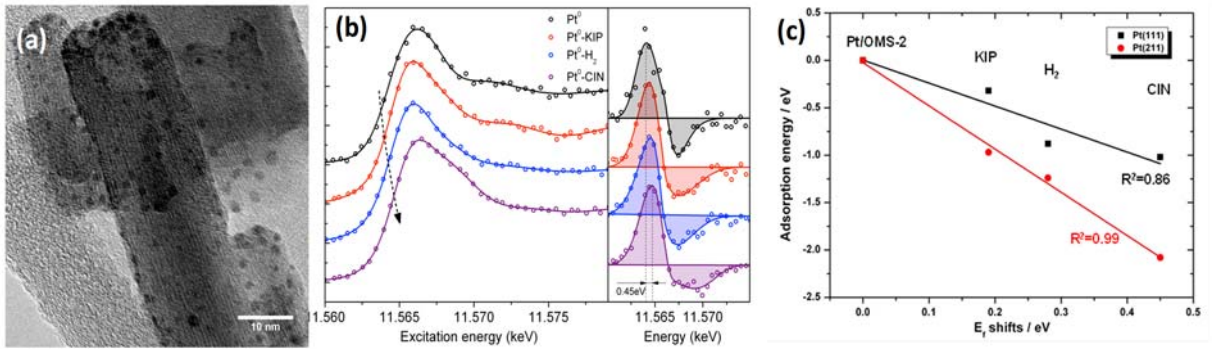


Figure 2. (a) HR-TEM image of 5 wt% Pt/OMS-2, (b) Pt LIII edge HERFD-XANES spectra of Pt/OMS-2 interacting with H2, KIP and CIN and corresponding shifts in the Fermi energy (Ef). (c) Correlation between the experimentally measure shifts in the HERFD-XANES spectra and the calculated adsorption energies from DFT for the Pt(111) and Pt(211) surfaces.

In summary, by using exemplar chemical processes, we have attempted to establish rational catalyst design criteria for development of novel catalysts and sustainable chemical processes to address imminent global challenges faced by our society.

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